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APPLICATIONS TO NEGATIVE ION SOURCE PROCESSES

A. M. Karo
J. R. Hiskes
R. J. Hardy

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VIBRATIONAL RELAXATION IN H_2 MOLECULES BY WALL COLLISIONS:
APPLICATIONS TO NEGATIVE ION SOURCE PROCESSES

A. M. Karo and J. R. Hiskes
Lawrence Livermore National Laboratory
Livermore, California 94550

and

R. J. Hardy
University of Nebraska
Lincoln, Nebraska 68588

Abstract

In the volume of a hydrogen discharge, H_2 molecules, excited to high vibrational levels ($v'' > 6$), are formed either by fast-electron collisions or from H_2^+ ions that are accelerated across the discharge-wall potential that undergo Auger neutralization prior to impact with the discharge chamber wall. We have used computer molecular dynamics to study the de-excitation and re-excitation of vibrationally-excited H_2 molecules undergoing repeated wall collisions. The initial translational energies range from thermal to 100 eV and the initial vibrational states range from $v'' = 2$ to $v'' = 12$. The average loss or gain of vibrational, rotational, translational, and total molecular energies and the survival rates of the molecules have been evaluated. At thermal energies vibrational de-excitation is the predominant process, and a consistent picture emerges of rapid energy redistribution into all the molecular degrees of freedom and a slower rate of loss of total molecular energy to the wall. At higher translational energies (1-100 eV) a substantial fraction of the molecules survive with large ($v'' > 6$) vibrational energy. This vibrational population provides a contribution to the total excited vibrational population comparable to that from the fast-electron

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collision process. Implications of these results for negative ion generation will be discussed.

I. INTRODUCTION

In the volume of a hydrogen discharge H_2 molecules are present that have been excited to high vibrational levels ($v'' > 6$). These are created either by fast-electron collisions or from H_2^+ ions that have been accelerated across the discharge-wall potential, undergoing Auger neutralization immediately before impact with the discharge chamber wall. These vibrationally-excited molecules are the source of negative ions through their dissociative attachment to electrons. At lower, thermal, energies de-excitation of the vibrationally-excited molecules at the walls will be an important loss mechanism leading to a reduction in their concentration in the discharge. In the case of H_2^+ wall collisions we require information about the fraction of incident ions that reflect from the wall as vibrationally-excited molecules. Depending on the discharge parameters either the electronic excitation or the H_2^+ Auger neutralization will be the dominant source of vibrational excitation.

During the past several years we have carried out an extensive series of computer experiments using a molecular dynamics approach designed to monitor the response of vibrationally-excited H_2 molecules undergoing collisions with a surface composed of Fe atoms and with impact energies corresponding to thermal, i.e., low energy (500-1500 K), translational kinetic energies.¹⁻³ From a statistical analysis of a large number of these classical trajectories, we have obtained qualitative estimates of the average loss of vibrational energy as a function of the number of collisions with the wall. Qualitative estimates of the rates of energy exchange and, therefore, of the extent of equipartition, i.e., the equilibrium distribution of total energy among the degrees of freedom of the molecular system, have been obtained from the calculations. We also have obtained estimates of the accommodation coefficient or the average transfer of energy between the molecules and the wall.

In these low-energy wall collisions there are a number of parameters describing the initial conditions whose values could perhaps affect to some extent the energy transfer rate from the vibrational to the other degrees of freedom or to the wall. For example, the accommodation rate is only of the order of a few percent for an interaction in which the binding energy between the molecule and the wall is small and the difference in molecule and wall masses large but would be expected to increase with the strength of the surface interaction. On the other hand, the physical or chemical nature of the interaction of the molecule with the surface will not dramatically affect the equipartition rate, which is already very rapid for fairly weak molecule-surface interactions, requiring only a few collisions to attain a high degree of equipartition. Additional calculations showed that these rates are not sensitive to different initial translational energies corresponding to plasma temperatures between 500 K and 1500 K or to initial choices of rotational states above the $J = 1$ state predominating at 500 K. Finally, because the initial vibrational states being considered correspond to energies of several electron volts, the wall temperature chosen does not have any significant effect.

In addition to investigating these low-energy, thermal wall collisions, we have recently begun to study collisions in which the translational energies can range up to 50 to 100 eV. These higher energies are of interest since H_2^+ molecular ions are formed in the volume of a hydrogen discharge with an equilibrium concentration in a high-power, high-density discharge typically ranging from twenty to thirty percent of the total electron density,⁴ and up to eighty percent for certain RF source configurations.⁵ Plasma potentials are typically in the range between 2-20 eV. These molecular ions are accelerated across this potential and neutralized prior to striking the wall by means of a two-step Auger neutralization process that we have proposed and discussed in more detail in an earlier paper.⁶ Briefly, in the first step of the process, as the H_2^+ ion approaches within 10 Å of the discharge wall, an electron from the surface is captured into the first excited $^3\Sigma_u$ electronic state. Because the vibrational levels of

the H_2^+ ions in the discharge are heavily populated throughout the first five levels, the H_2 ($^3\Sigma_u$) state will be formed over a range of internuclear separations ranging from less than 0.5 Å to more than 1.2 Å. Since the $^3\Sigma_u$ state is repulsive, the two nuclei begin to separate as the molecule continues to approach the surface. After moving in another 2-5 Å, a second electron is captured directly to the ground state ejecting the $^3\Sigma_u$ orbital electron. At this point, however, the molecule has expanded to a larger internuclear separation, and the ground electronic $^1\Sigma_g^+$ state is created preferentially with $v'' > 0$. By this sequence neutral molecules are formed in high vibrational states and strike the wall with translational kinetic energies corresponding to the discharge-wall potential.

An extensive series of molecular dynamics trajectory calculations has now been completed with the purpose of determining the probability of survival of such vibrationally-excited H_2 molecules after undergoing high-energy collisions with a wall composed of Fe atoms. Since the total energies ($E_{vib} + E_{rot} + E_{trans}$) are far in excess of the molecular binding energy (4.75 eV), there will be an interesting interplay between dynamical pathways leading to vibrotational de-excitation and re-excitation and those leading to dissociation to free atoms. Penetration of the wall by hydrogen molecules at these higher translational energies has not been found to occur, but single-atom penetration for energies ≥ 10 eV does occur occasionally and is included in the dynamics, often leading to microscopic sputtering of Fe atoms from the wall. Although the experimental upper limit for translational impact energy is around 20 eV, a number of trajectories for translational kinetic energies up to 100 eV have also been considered in order to establish an approximate upper bound on the translational energy above which the probability for molecular survival would be vanishingly small.

Finally, our codes have also been used to study the 2 eV Frank-Condon neutral hydrogen atoms produced in the plasma as they undergo collisions with a 500 K Fe wall. The results we have obtained from a large number of trajectories indicate that at this energy about 80 percent of the incident atoms are reflected from the wall. These studies are being extended to include both higher and lower energies and other wall conditions.

II. COMPUTATIONAL METHOD

Computer molecular dynamics has evolved to become a flexible and useful modeling technique because of the availability of modern high-speed computers and because of the complementary development of sophisticated software including, in particular, efficient algorithms for solving coupled nonlinear second-order differential equations and the ready use of high-precision computer graphics. In the classical approach which characterizes most molecular dynamics simulations, we monitor the detailed evolution of the system by solving Newton's Second Law equations of motion for all the atoms comprising the active regions of the assembly. As a result, the coordinates and velocities are obtained as functions of time. The initial positions and velocities of the particles represent the initial conditions on these equations.

It then remains only to define the forces acting on each of the particles. The force acting on any one particle is the resultant of its interactions with all other atoms in its neighborhood. In principle, it should be obtained as the derivative of an effective many-body potential. However, calculations that would require part or all of a complete potential energy hypersurface are at a level of difficulty far beyond present considerations. Fortunately, the usual sum-of-pair-potentials approximation to the potential energy surface should be adequate for the accuracy needed in the present calculations. To obtain solutions for the equations of motion of our dynamical system, the set of coupled nonlinear, second-order differential equations that represent the forces are reduced to a double set of first-order ordinary differential equations by standard procedures. For the numerical solution of this set of equations, we have used the variable-step, variable-order, implicit Adams' method with functional (or fixed-point) iteration; this is a generalization of the classical Adams-Bashforth-Moulton method.⁷ Relative error buildup is controlled by an error tolerance parameter, so that numerical error is typically kept to less than one part in a million for times up to 10-50 picoseconds during a simulation.

In summary, subject to constraints imposed by using an essentially classical approach and by practical computational limits on the number of

particles in a dynamical ensemble (10^3 to 10^4) and on the period of time over which the system can be followed (10^3 to 10^4 in natural time units, or 10^5 to 10^7 integration steps), we have a powerful calculational method at our disposal for examining the microscopic dynamics of a variety of particle-surface phenomena, including the elementary reactive processes underlying such diverse phenomena as corrosion, combustion, and heterogeneous catalysis.^{8,9}

III. DESCRIPTION OF THE MODEL

As indicated in the preceding Section, an underlying assumption in the calculations that have been carried out to date is that the essential dynamics can be obtained within the sum-of-pair-potentials approximation. That this is reasonable has been checked by varying the surface-molecule potential over a wide range and noting only slight changes in the statistical results. For the FeH interaction we have used a modification of the two-body potential of Scott and Richards¹⁰ in which we have reduced the strength of the interaction by factors of 5 or more, thus simulating the weaker pair interaction seen by a hydrogen molecule approaching a cluster of Fe atoms. An FeH effective "cluster" two-body potential obtained from unrestricted Hartree-Fock ab initio calculations on Fe_4H clusters¹¹ gave results that were not significantly different statistically from the "reduced" diatomic potential obtained from Scott and Richards. For the Fe potential we have used a Morse potential fit to the two-body potential obtained by Johnson in fitting experimental elastic-constant data.¹² A Morse fit to the experimental H_2 potential curve can be accurately made up to the $v'' = 8$ or 9 level. Beyond that the Morse curve rises more slowly at large internuclear separations. Therefore, at very large vibrational excitations the period of time spent by the molecule in its stretched configuration will be in reality somewhat less than in our simulations, but this should have a minor effect on the results above $v'' = 8$ and none for $v'' \leq 8$. In Figure 1 we display the pair potentials that have been used in our simulations.

Both two- and three-dimensional trajectory calculations have been considered in our studies. Because of cost we have carried out many more two-dimensional calculations from which we have obtained a statistically-significant qualitative understanding of vibrational de-excitation and re-excitation as well as of the redistribution of large initial vibrational and/or translational energies into other degrees of freedom following repeated wall collisions. As a check, a smaller number of three-dimensional calculations have been carried out. Since additional translational, rotational, and vibrational degrees of freedom are present, it is important to evaluate at least qualitatively whether or not these have any significant or unexpected effect on the rate of vibrational de-excitation, or re-excitation at higher impact energies; on the rate of accommodation of the total molecular energy with the temperature of the wall as the system approaches thermal equilibrium; or on the rate of approach of the mean vibrational, rotational, and translational energies to statistical equilibrium, i.e., equipartition among the available degrees of freedom.

Figure 2 shows schematically the initial configurations for either a two-dimensional or a three-dimensional situation. These are correlated in our simulations in the sense that the two-dimensional case represents a constrained three-dimensional situation. It can be seen that the two-dimensional trajectories are those that are restricted to a plane that includes one of the (100) planes of the face-centered-cubic Fe lattice. In Figure 3 we show in more detail the initial configuration for a two-dimensional trajectory in which the angle of incidence to the wall is 30° and the initial angle of the bond with respect to the wall (the "phase" of the molecule) is 120° .

A sample trajectory is shown in Figure 4. Here the translational velocity corresponds to the average molecular speed associated with a plasma temperature around 500 K while the rotational motion that has been assigned corresponds to the predominant $J = 1$ state. The initial separation of the H atoms corresponds to the $v'' = 6$ level, about $23,240 \text{ cm}^{-1}$ above the potential energy minimum. At some initial time, $t = 0$ (in units of 10^{-14} seconds), the hydrogen molecule has been set in motion toward the lattice composed of iron atoms. The wall in this simulation represents a

surface layer and four interior layers with an initial temperature of 500 K. Because of the large mass difference between the molecule and wall, the number of atoms chosen to represent the wall should be more than sufficient. In Figure 4a the molecule has begun to interact very weakly with the wall after having moved toward it for 0.21 picoseconds (ps). The hydrogen atoms are close together, near the inner turning point, and the molecular state is, consequently, helium-like. At 0.30 ps additional weak bonds have formed and the molecule is now stretched and in a state that can be described in terms of two weakly-bonded hydrogen atoms. This is shown in Figure 4b. In Figure 4c, at 0.32 ps, a strong bond has begun to form between the molecule and one of the surface atoms. A sequence of strong dynamical interactions then occurs during the next 0.08 ps during which time the molecule strongly interacts with the wall while undergoing some eight vibrational oscillations. In figure 4d the molecule is shown receding from the surface; vibrational energy has been transferred to rotational and translational motion. Although there has been a major redistribution of energy among the degrees of freedom of the molecule, only some 3 to 4 percent of the total molecular energy has been given up to the surface, principally because of the mass difference between molecule and surface atoms.

IV. VIBRATIONAL RELAXATION AND EQUIPARTITION IN LOW-ENERGY (500 K) H_2 -SURFACE COLLISIONS

We have examined the dynamical behavior of molecules given various initial vibrational energies corresponding to $v'' = 2$ up to $v'' = 14$ during repeated collisions with the Fe surface. Since molecular energies found in typical hydrogen discharges are in the range of 500-1500 K, we have taken 500 K as the initial translational temperature and $J = 1$ as the predominant rotational state at this temperature. Because the translational energies and the energies of the predominant rotational states are much less than any vibrational excitation, the dynamics of vibrational de-excitation should be relatively insensitive to these as well as other initial conditions in this temperature range. Finally, the Fe atoms making up the wall have been given initial random velocities corresponding to a local kinetic temperature of 500 K.

With initial conditions for the model systems appropriately chosen, a computer run consists of repeated molecular collisions with the wall for a specified number of bounces. A new H_2 molecule is then chosen with random position and phase, and a new set of trajectories calculated. This sequence is repeated until the run is finished. Wall capture or dissociation at these low translational energies are exceedingly rare events; the few (<1%) cases observed have occurred only after a large number ($>>10$) of wall collisions have taken place. Upon capture by the wall or when dissociation occurs, a trajectory is automatically terminated.

We have shown that after successive collisions the attenuation and relaxation of the uppermost portion of the vibrational spectrum can be approximated by an exponential decay of the form¹³

$$e^{-c/b(v'')} \quad (1)$$

where c is the collision number and $b(v'')$ the decay constant. Since $b(v'')$ ranges from two to four for $v'' \leq 4$ to near unity for $v'' \geq 12$, we have found it necessary to consider a maximum of 20 bounces for initial excitations corresponding to $v'' = 2$, but only 5 bounces for $v'' \geq 8$. Thus, if no capture or dissociation were to occur, a computer run of 10 sets of trajectories would consist of from 50 to 200 individual trajectories, made up of 10 "first bounce" collisions with the wall, 10 "second-bounce" collisions, and so on. In addition, equipartition among the molecular degrees of freedom is approached rapidly in all cases and is nearly reached on a statistical basis after four or five collisions.

Results for de-excitation and equipartition as a function of collision number are displayed in Figures 5, 6, and 7 for several hundred molecules initially in the $v'' = 12$, $J = 1$ vibrotational state and with translational velocities equal to the average molecular speed of a 500 K gas. In Figure 5 it can be seen that the result of successive wall collisions is a de-excitation and broadening of the vibrational population distribution. The wall collisions are accompanied by a small fractional loss of the total molecular energy to the wall as the molecules accommodate to the energy of the wall, but there is a considerable change in rotational and translational

energy. As shown in Figures 5-7, the mean values for the vibrational, rotational, and translational energies approach statistical equipartition among the degrees of freedom while maintaining a broad distribution in each of these degrees of freedom.

These results have been analyzed more quantitatively by considering at each bounce the deviations D of the molecular energy from equipartition.³ The assumption is made that at each bounce on the average the deviation from equipartition is reduced by a fixed fraction f of the deviation. The value for this fractional adjustment is obtained by a least squares fitting of the following expressions for D to data from the successive wall collisions:

$$D_n = D_0 (1 - f)^c, \quad (2)$$

where for one of the individual degrees of freedom

$$D_n^{\text{individual}} = E_n^{\text{individual}} - p/2 \left(k T_n^{H_2} \right) \quad (3)$$

and for the total energy,

$$D_n^{\text{total}} = E_n^{\text{total}} - 5/2 \left(k T^{\text{wall}} \right), \quad (4)$$

where p represents the number of degrees of freedom for vibration, rotation, or translation, and where the molecular temperature is given by

$$T_n^{H_2} = T^{\text{wall}} + \frac{2D_0^{\text{total}} (1 - f^{\text{total}})^c}{5k} \quad (5)$$

In Table I we give results for the fractional adjustments of the deviation from equipartition for the total energy and for the vibrational, rotational, and translational energies. The least squares fitting has been made in each case to the first five wall collisions. Values for $f(\text{total})$ give essentially the rates of accommodation, and it can be seen that on the average only three to four percent of the molecular energy is being

transferred to the wall during each collision. The large values (fifty to seventy percent) for the other fractional adjustments give an indication of the rapid equipartitioning of energy among the molecular degrees of freedom.

V. VIBRATIONAL EXCITATION AND DE-EXCITATION OF H_2 MOLECULES BY H_2^+ WALL COLLISIONS

In a high-power, high-density hydrogen discharge H_2^+ molecular ions are formed in equilibrium concentrations that reach from twenty to thirty percent of the total electron density.⁴ Under normal operation the discharge assumes a positive potential normally in the range from several volts up to 20 volts relative to the walls. The result is that these ions will strike the discharge chamber walls with a kinetic energy equal to the plasma potential. We have described previously⁶ a three-step process in which the H_2^+ ions are neutralized in a two-stage Auger process, followed by a third stage in which the now-neutral ground-state molecules strike the walls at these high translational energies. The overall result is that the incident ions will either be dissociated, forming free atoms that may reflect from the surface or be bound to the wall, or will be reflected from the wall as neutral molecules having a broad range of vibrational excitations.

The vibrationally-excited molecules that are reflected will contribute to the formation of negative ions by dissociative attachment to electrons. As is well known, H_2 molecules are also excited to high vibrational levels by fast-electron collisions, the E-V process, with the subsequent formation of negative ions, again by dissociative attachment. The extent to which the excited molecules generated from the H_2^+ molecular ions will contribute to negative ion formation will depend upon the fraction f_1 of incident molecules that survives the wall collisions and the fraction f_2 of these that is formed with $v'' \geq 6$. Thus, the product $f_1 f_2$ gives the fraction of incident H_2^+ surviving as $H_2(v'' \geq 6)$.

In order to estimate the contribution of the three-step neutralization process to the formation of vibrationally-excited neutrals, we have calculated a large number of wall-collision trajectories, varying the

initial angle of impact of the H_2 molecule with the wall from 0 to 30° , the initial state of vibrational excitation from $v'' = 2$ to $v'' = 12$, and the translational energy from 1 to 20 eV. In addition, to determine an effective upper limit for an impact energy where the probability of survival of the molecule would become essentially zero, we have calculated a considerable number of trajectories at 50 and 100 eV. The results of these calculations are summarized in Table II.

The product $f_1 f_2$ can be seen to be consistently in the range 0.1 to 0.2. We have previously compared the rates of $H_2(v'' \geq 6)$ formation for both the E-V process and the H_2^+ wall neutralization process, making reasonable assumptions about the electron and gas densities, the ratio of H_2^+ to electron densities, and the ratio of the fast electron density to the total electron density. We found that when the product $f_1 f_2$ is around 0.15, the two processes contribute equally to $H_2(v'' \geq 6)$ formation for the lower gas densities. From Table II we again can conclude that at lower gas pressures, the wall recombination of H_2^+ to form $H_2(v'' \geq 6)$ will make a contribution to the total vibrational excitation and, hence, to the negative ion yield that is comparable to that from the E-V process. For the higher H_2^+ concentrations found in RF sources, the wall recombination process may, in fact, dominate.

VI. CONCLUSIONS

In this report we have illustrated how computer molecular dynamics can be applied to obtain information in a situation where experimental data is very difficult to obtain: the vibrational de-excitation of highly-excited molecular systems during wall collisions. We have been able to obtain results for the average loss or gain of vibrational, rotational, translational, and total energy during repeated collision with a wall. We have seen that these collisions provide an effective and rapid kinematic mechanism for energy transfer between the molecular degrees of freedom. We have found that after the first or second collision with a surface, during which about half the initial vibrational energy is lost to rotational excitation and translational motion, subsequent collisions can result either in further vibrational de-excitation, with additional increases in the rotational and

translational energies, or in vibrational re-excitation to higher-lying states accompanied by corresponding decreases in rotational and translational energies.

The occurrence in nearly every case of rotational excitation from the initial $J = 1$ state up to very large values, $J \geq 14$, has recently prompted an investigation of dissociative attachment rates not only as a function of v'' but also of J .¹⁴ By including these higher rotational states in the calculations of rotational dissociative attachment rates, it was found that the rate of dissociative attachment is increased by a factor of two for the $v'' = 6$ level, but there is only a fifty percent increase for the $v'' = 7$ level. Rates for higher vibrational levels are not significantly affected. Overall, the concentration of negative ions is estimated to be increased by thirty-five to fifty percent because of the presence of rotational excitation in these vibrationally excited species.

In summary, we have surveyed several thousand classical two-dimensional trajectory calculations at thermal energies and have checked the qualitative conclusions against a number of three-dimensional calculations. On the average the total energy possessed by H_2 molecules initially vibrationally excited is transferred only to a slight extent to a wall composed of heavy atoms such as Fe, presumably because of the substantial mass mismatch between the molecule and the surface atoms. However, wall collisions do provide an excellent mechanism for vibrational energy transfer to rotation and translation. Rotational excitation occurs rapidly from the initial $J = 1$ state to states with very large J values in nearly every first collision of the molecule with the wall. As a consequence, vibrational de-excitation is also most marked during the first collision as the vibrational energy is redistributed to rotation and translation. We have also found from a preliminary series of calculations that when H_2 molecules are initially in the $v'' = 2$, $J = 1$ vibrotational state, approximately eight to ten wall collisions are required before relaxation to the $v = 0$ state is achieved. This de-excitation rate is consistent with the rate deduced from the analysis of $v'' = 1, 2$ populations measured using coherent anti-stokes Raman scattering techniques.

The loss of total molecular energy to the wall (accommodation) is found to be in the three to four percent range, whereas energy redistribution leading to equipartition among the vibrational, rotational, and translational degrees of freedom of the molecule occurs very rapidly and is essentially achieved after three or four collisions with the surface. For most collisions, the H_2 molecule is in near proximity and strongly interacting with the wall for only a few vibrational periods.

At higher translational energies (1 - 20 eV), a substantial fraction of molecules lying in high vibrational states ($v'' \geq 6$) are found to survive surface collisions, rebounding from the surface in a broad spectrum of vibrational levels. A significant fraction of these are in high-lying vibrational states. Molecules in lower-lying vibrational states that impact the wall with large translational kinetic energies can also be readily re-excited to higher vibrational levels. Thus, the process of the wall recombination of H_2^+ to form $H_2(v'' \geq 6)$ can make an important contribution to the total vibrational excited population and to the negative ion yield comparable to that from the fast-electron process.

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Table I. Fractional adjustments of the deviation from equipartition for Molecules undergoing five wall collisions. The mean error is also given.

| $v'' = 8, J = 1$ (1500 trajectories) | | | |
|--------------------------------------|-----------------------|----------------------|-------------------------|
| $f(\text{total})$ | $f(\text{vibration})$ | $f(\text{rotation})$ | $f(\text{translation})$ |
| 0.0352 ± 0.0095 | 0.645 ± 0.071 | 0.628 ± 0.146 | 0.715 ± 0.110 |
| $v'' = 12, J = 1$ (500 trajectories) | | | |
| $f(\text{total})$ | $f(\text{vibration})$ | $f(\text{rotation})$ | $f(\text{translation})$ |
| 0.0325 ± 0.0072 | 0.535 ± 0.091 | 0.468 ± 0.084 | 0.624 ± 0.107 |

Table II. Fraction f_1 of molecules surviving a wall collision at higher impact energies. The fraction of the surviving molecules with $v'' > 6$ is f_2 .

| E_{normal} | | v'' | | | | | | | | |
|---------------------|-----|-------|-------|-----------|-------|-------|-----------|-------|-------|-----------|
| | | 2 | | | 8 | | | 12 | | |
| | | f_1 | f_2 | $f_1 f_2$ | f_1 | f_2 | $f_1 f_2$ | f_1 | f_2 | $f_1 f_2$ |
| 1 eV | 0° | 1.00 | .00 | .00 | 1.00 | .47 | .47 | .60 | .50 | .30 |
| | 15° | 1.00 | .00 | .00 | 1.00 | .38 | .38 | .56 | .54 | .30 |
| | 30° | 1.00 | .00 | .00 | 1.00 | .40 | .40 | .61 | .30 | .18 |
| 4 eV | 0° | .92 | .13 | .12 | .38 | .32 | .12 | .64 | .28 | .18 |
| | 15° | .94 | .16 | .15 | .48 | .54 | .26 | .64 | .22 | .14 |
| | 30° | .71 | .13 | .09 | .45 | .58 | .26 | .65 | .38 | .25 |
| 10 eV | 0° | .42 | .57 | .24 | .20 | .83 | .17 | .18 | .89 | .16 |
| | 10° | .27 | .73 | .20 | .15 | .67 | .10 | .14 | .86 | .12 |
| | 20° | .33 | .10 | .03 | .20 | .92 | .18 | .23 | .43 | .10 |
| 20 eV | 0° | .30 | .60 | .18 | .27 | .50 | .14 | .05 | .50 | .03 |
| | 10° | .12 | .50 | .06 | .21 | .50 | .10 | .13 | .38 | .05 |
| | 20° | .28 | .29 | .08 | .20 | .20 | .04 | .13 | .60 | .08 |

FIGURE CAPTIONS

- Figure 1. Pair potentials for the interactions between atoms.
- Figure 2. Comparison of 2D and 3D model systems.
- Figure 3. A typical starting configuration for an H_2 molecule moving toward a wall at velocity v , phase angle α , and angle θ from the normal.
- Figure 4. Sample trajectory for an H_2 molecule ($v'' = 6$, $J = 1$) colliding with an Fe lattice at 500 K.
- Figure 5. Distribution of vibrational energy as a function of successive wall collisions for H_2 molecules initially in the $v'' = 12$, $J = 1$ vibrotational state.
- Figure 6. Distribution of rotational energy as a function of successive wall collisions for H_2 molecules initially in the $v'' = 12$, $J = 1$ vibrotational state.
- Figure 7. Distribution of translational energy as a function of successive wall collisions for H_2 molecules with an initial translational velocity corresponding to the average molecular velocity at 500 K.

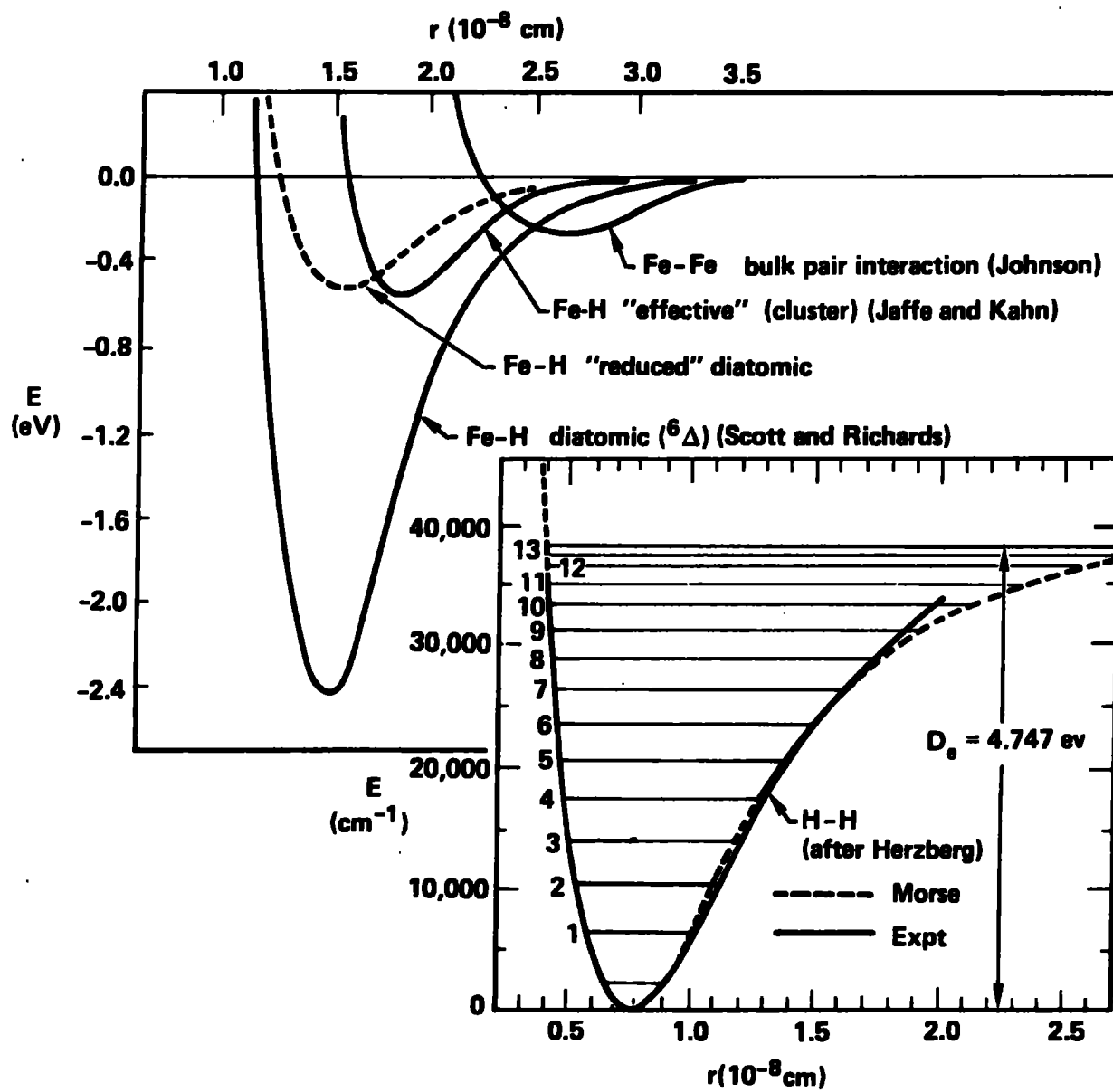
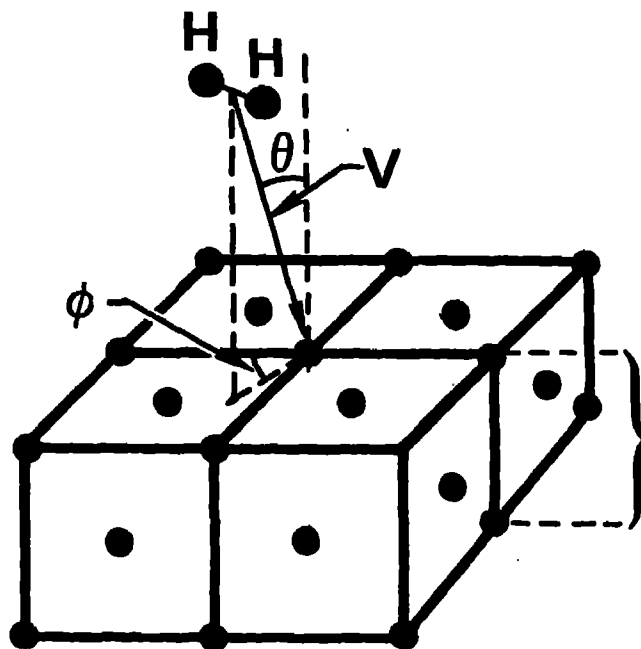


Figure 1

3D system



2D system

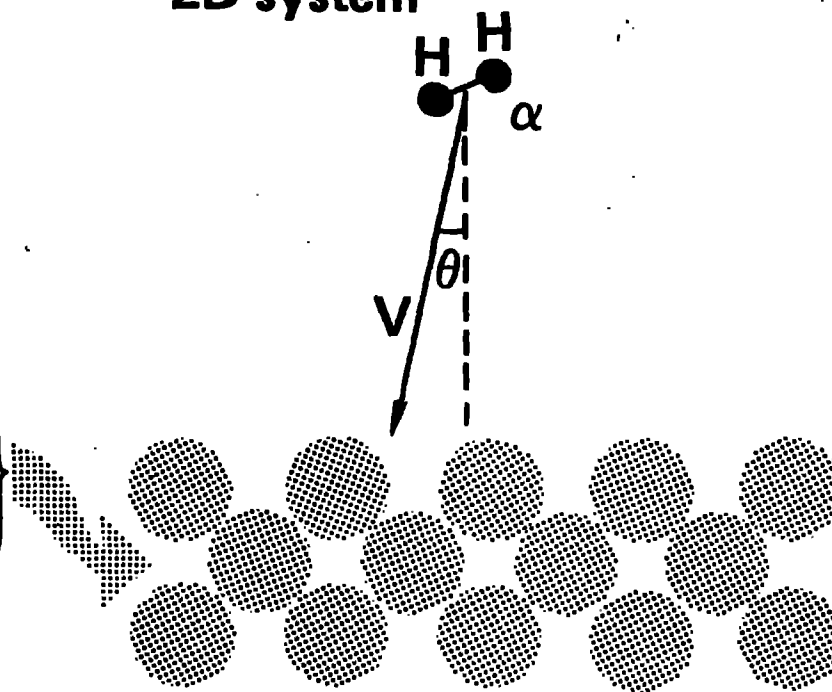


Figure 2

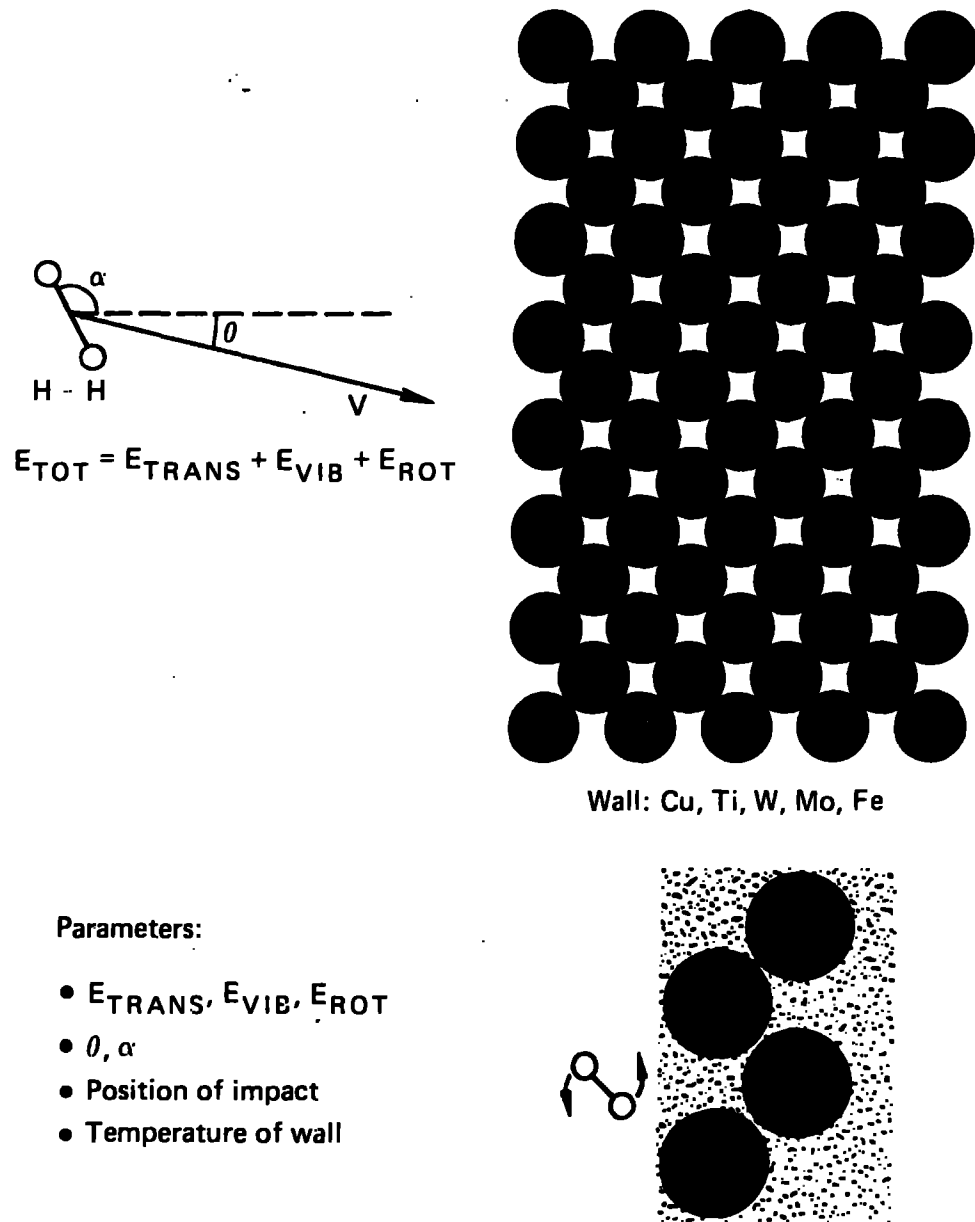


Figure 3

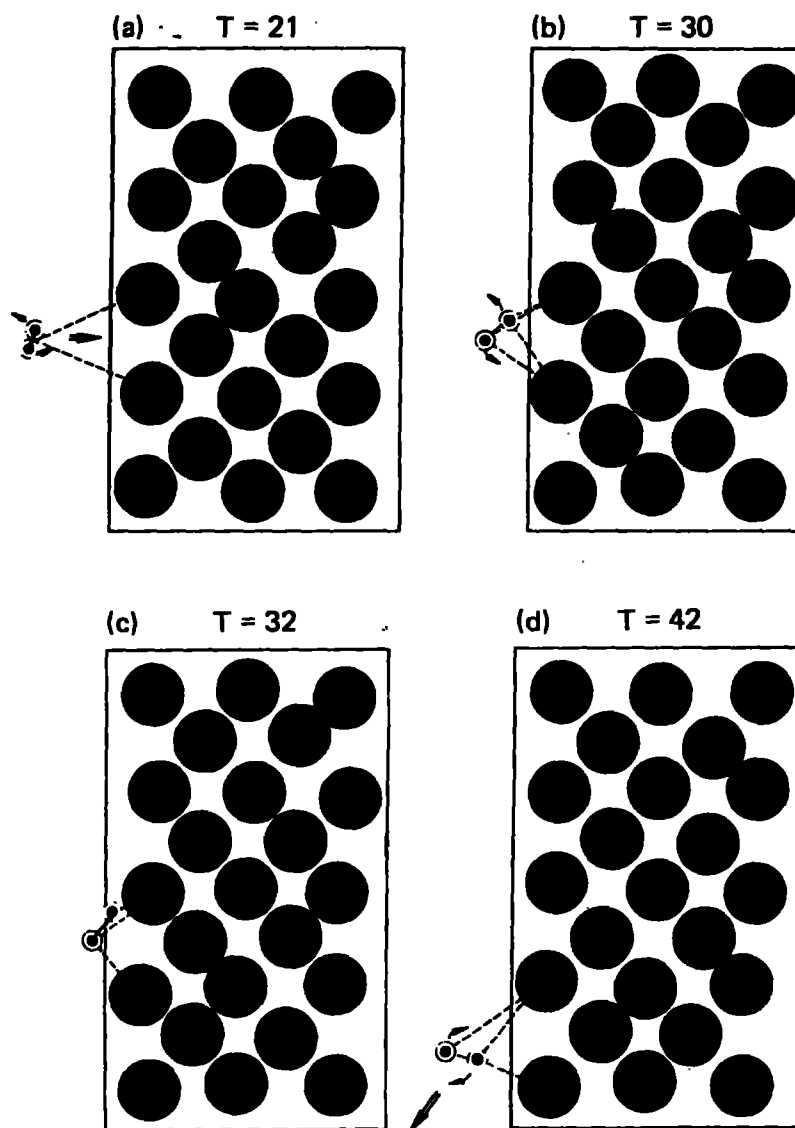


Figure 4

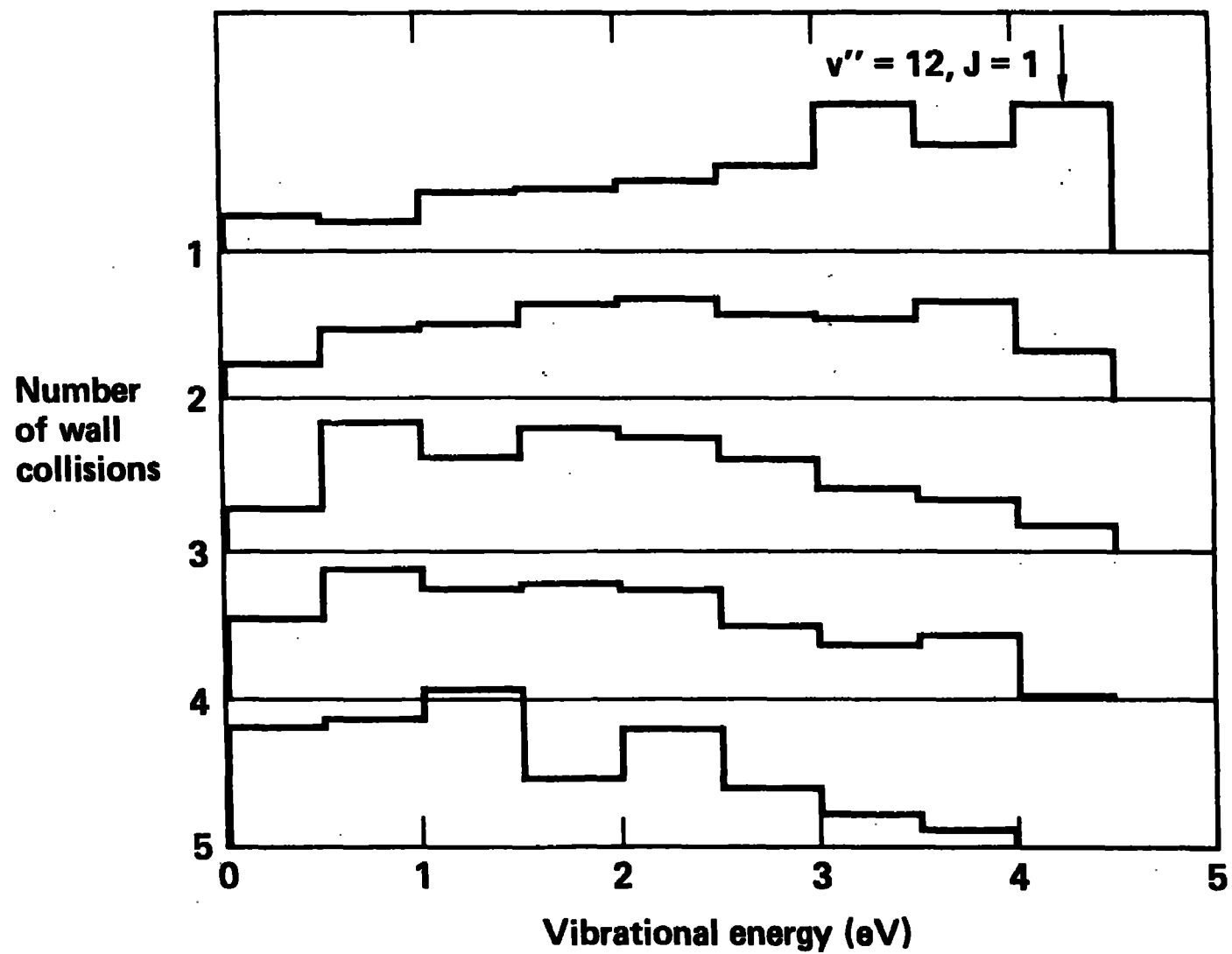


Figure 5

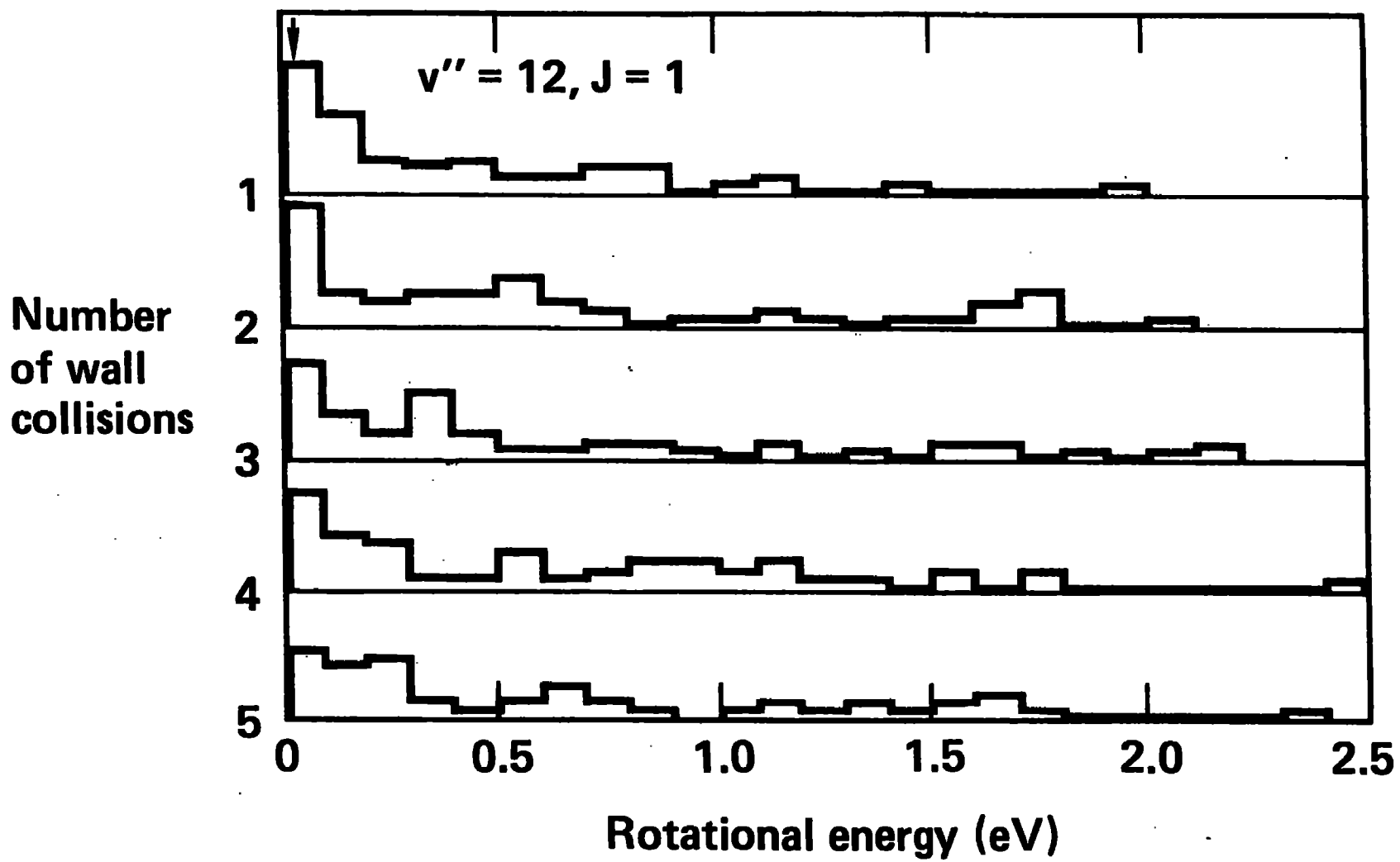


Figure 6

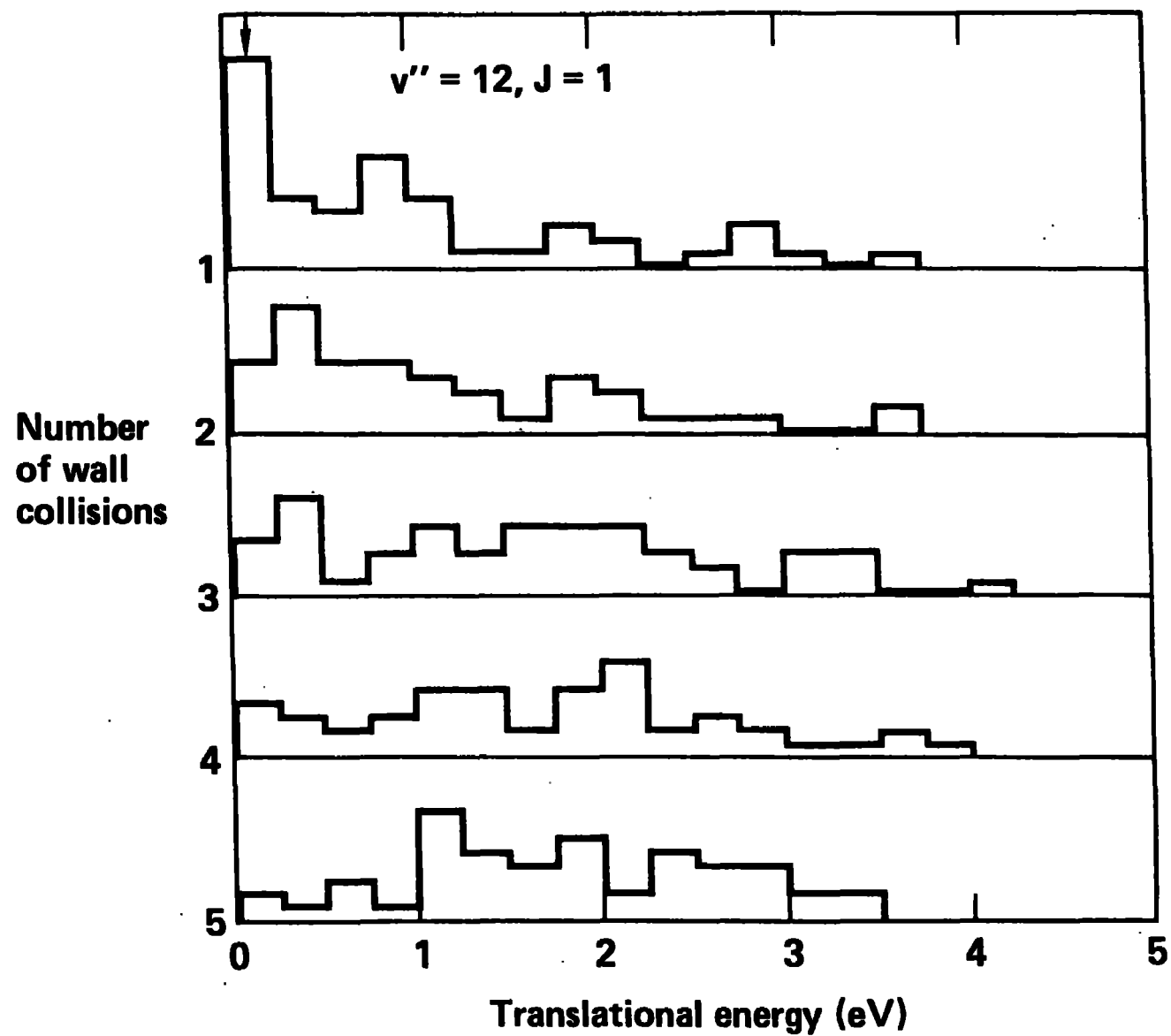


Figure 7